

Abstract

Power ultrasound enhances the rates of chemical reactions through an indirect phenomenon, namely acoustic cavitation, which is the formation, growth, and collapse of bubbles in an alternating pressure field. The implosive collapse of bubbles causes intense local heating (5000°K) and high pressures (500 atm). Under these extreme conditions, the contents of the bubble fragment to yield high energy free radicals. The reactive intermediates, once released into the bulk of the liquid, react with other species present.

Most of the sonochemical reactions on a laboratory scale have been carried out predominantly with horn type sonicators. A systematic study of the effect of reactor shape on the sonochemical yields of reaction products is therefore not available. Further, there have been no reports on correlation between batch reactor data and operation of the same reactor in a continuous mode. The present work was aimed at studying these two concepts. Sonochemical decomposition of aqueous solutions of CCl_4 , which leads to the formation of Cl_2 in the bubble phase was selected for study, and the extent of decomposition was measured by I_2 released, which is formed by the reaction of Cl_2 with KI present in the solution. The experiments were carried out with cylindrical and spherical reactors, wherein the reactor walls were subjected to ultrasonic vibrations by a piezoelectric crystal. The effect of the length to diameter ratio, and frequency on the sonochemical yields of I_2 was studied with two cylindrical reactors of capacities 250 ml and 600 ml. It was found that good cavitation patterns were observed only in a narrow range of frequencies. These correspond to normal as well as coupled radial and longitudinal modes of the crystal, and were around 53, 110, and 170 kHz. Experiments were carried out at around 110 kHz to avoid damage to the crystal. The trend observed in the concentration of I_2 liberated, amount of I_2 generated, and sonochemical yields for various liquid volumes

investigated in cylindrical reactors could not be explained through power input measurements. The normal modes of vibration of the presently studied cylindrical reactors were calculated. Several coupled normal modes exist around the operational frequency 100 kHz. Hence, resonance between the various coupled modes of the reactor and the transducer occurred for all the liquid volumes investigated and the experimental trend in the sonochemical yields could not be explained through resonance. This suggests that the determination of spatial distribution of pressure field in the reactor might be needed to account for the observed trend.

Based on the data with batch experiments, the performance of a small scale cylindrical reactor (250 ml) operating in continuous mode could be predicted satisfactorily for large residence times.

Experiments on spherical reactors were carried out with two spherical flasks of capacities 260 ml and 130 ml. Different liquid volumes were used here as well. As observed with cylindrical reactors, the sonochemical yields for various liquid volumes could not be explained through power input measurements. However, fully filled reactors showed maximum sonochemical yields. The radial resonant modes of vibration of a completely filled spherical flask were calculated and were found to be resonant with the operational frequencies. The observations made for complete spherical volumes could therefore be explained based on the phenomenon of resonance.

The effect of driving the reactor at identical as well as at different frequencies, and at varying intensities on sonochemical yields of I_2 was studied with 130 ml spherical reactor. Two different relative positions of the transducers were also investigated. The sonochemical yields for both positions, but at identical voltage input to the crystals were more compared to the single crystal experiments. It could be concluded that power utilization was more efficient for the bifrequency operation of the reactors.